Generalized f / P, Z_T and Z_P Values for Liquids at Low Reduced Temperatures

The three-parameter correlation of Pitzer et al. for fugacity coefficients (f/P) has been extended to liquids in the $0.5 \leq T_r \leq 0.8$ and $0.2 \leq P_r \leq 9.0$ region. In addition, values of the derivative compressibility factors Z_T and Z_P have also been obtained in the same region. This extension is based on the generalized correlation of the compressibility factor Z recently reported. The isothermal coefficient of bulk compressibility β_T compiled by Rowlinson has been employed with the pressure effect on β_T taken into consideration. The correlation for f/P obtained in this work is compared with that of Curl and Pitzer at $T_r = 0.8$, Chao et al. at T_r from 0.50 to 0.70, and that of Carruth and Kobayashi in the $0.50 \leq T_r \leq 0.64$ region. Using the tabulated Z_P and Z_T values $\frac{H^* - H}{T_c}$, $\left(\frac{\partial V}{\partial P}\right)_T$, and $\left(\frac{\partial V}{\partial T}\right)_P$ have been calculated and compared satisfactorily with the corresponding values derived from literature data. In addition, a correlation of vapor pressures of both hydrocarbons and nonhydrocarbons is also presented. The agreement between this correlation and those reported by Pitzer et al. and Carruth and Kobayashi is very satisfactory.

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Knowledge of the thermodynamic properties of normal fluids at extreme conditions of low temperature and high pressure is important in the design of low temperature gas separation and liquefaction plants. Relatively little experimental information has been found available at low temperatures for those thermodynamic properties which involve the effects of pressure and temperature on volume. The fundamental quantity which can be used for obtaining these partial derivatives of volume is the compressibility factor Z. A generalized correlation of Z which extends the correlation of Pitzer et al. to low temperatures has been recently reported for predicting the volumetric properties of normal fluids. The purpose of this investigation is to utilize this extended correlation to evaluate and generalize at low temperatures the liquid phase fugacity coefficient (f_l/P), and the derivative compressibility factors Z_P and Z_T of Reid and Valbert which can be readily related to numerous thermodynamic properties.

CONCLUSIONS AND SIGNIFICANCE

The three-parameter correlation of Curl and Pitzer for calculating the liquid phase fugacity coefficient (f_l/P) has been extended to the low temperature region where $0.5 \leq T_r \leq 0.8$ and $0.2 \leq P_r \leq 9.0$. The correlated results of $\log (f_l/P)^{(0)}$ and $\log (f_l/P)^{(1)}$ are presented in tabular form for easy interpolation. These results agree well with those of Curl and Pitzer at $T_r = 0.8$, which is the lower limit of their correlation, and those of Carruth and Kobayashi in the $0.54 \leq T_r \leq 0.64$ region. They are smoother than those of Chao et al. at T_r from 0.50 to 0.70. Although some discrepancies, mainly in the $\log (f_l/P)^{(1)}$ function, are observed between this work and the values of Chao et al. and Carruth and Kobayashi at $T_r = 0.50$ and $T_r = 0.52$, the differences in (f_l/P) values are not considered to be significant.

In the determination of the pressure effect on liquid fugacity, vapor pressure values are required. In this investigation, vapor pressure data used included both hydrocarbons and nonhydrocarbons, while Chao et al. and Carruth and Kobayashi used only hydrocarbons.

The derivative compressibility factors of Reid and Valbert have also been extended to the same temperature and pressure region, and presented in tabular form. Values of Z_P and Z_T have been used to compute $\frac{H^* - H}{T_c}$, $\left(\frac{\partial V}{\partial P}\right)_T$ and $\left(\frac{\partial V}{\partial T}\right)_P$ values. The results of these calculations compare favorably with values derived from literature data, indicating the usefulness of the proposed values for engineering calculations.

Recently, a generalized correlation of the compressibility factor Z has been proposed (Lu et al., 1973) which extends the three-parameter correlation of Pitzer et al. (1955) from the $0.80 \leq T_r \leq 4.0$ and $0 \leq P_r \leq 9$ region to the $0.5 \leq T_r \leq 0.8$ and $0 \leq P_r \leq 9$ region. The purpose of this investigation is to evaluate and generalize, by means of the extended correlation, the liquid phase fugacity coefficient (f_l/P) and the derivative compressibility factors Z_P and Z_T of Reid and Valbert (1962) in the same low temperature region. These derivative compressibility factors are particularly useful for obtaining the partial derivatives of volumes with temperature or pressure, which may subsequently be used for obtaining other useful thermodynamic properties.

In the development of the extended correlation of Z, values of the isothermal coefficient of bulk compressibility β_T, compiled by Rowlinson (1969), were used in the evaluation of Z values of liquids, with the pressure effect on β_T taken into consideration. A test of the extended correlation with volumetric data for 21 compounds yields an average deviation of 1.63% in Z for the compressed liquids, which is a good indication of the reliability of

TABLE 1. VALUES OF LOG $P_r^{s(0)}$ AND LOG $P_r^{s(1)}$

T_r	$-\log P_r^{s(0)}$ This work	$-\log P_r^{s(0)}$ Pitzer et al.	$-\log P_r^{s(0)}$ Carruth and Kobayashi	$-\log P_r^{s(1)}$ This work	$-\log P_r^{s(1)}$ Pitzer et al.	$-\log P_r^{s(1)}$ Carruth and Kobayashi
0.50	2.333		2.315	2.826		2.962
0.52	2.149		2.130	2.526		2.660
0.54	1.982		1.965	2.273		2.370
0.56	1.823	1.834	1.818	2.061	2.08	2.120
0.58	1.679	1.688	1.680	1.867	1.88	1.908
0.60	1.543	1.552	1.544	1.688	1.70	1.710
0.62	1.420	1.426	1.424	1.518	1.54	1.545
0.64	1.307	1.308	1.308	1.343	1.39	1.390
0.66	1.199	1.198	1.198	1.206	1.25	1.250
0.68	1.099	1.096	1.096	1.078	1.12	1.120
0.70	1.000	1.000	1.000	1.000	1.00	1.000
0.72	0.908	0.909		0.880	0.895	
0.74	0.823	0.823		0.789	0.800	
0.76	0.740	0.742		0.709	0.705	
0.78	0.664	0.665		0.620	0.620	
0.80	0.591	0.592		0.542	0.545	

TABLE 2. VALUES OF $\log_{10}\left(\frac{f_l}{P}\right)^{(0)}$

$T_r \backslash P_r$	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
0.50	−1.621	−1.904	−2.062	−2.168	−2.247	−2.308	−2.357	−2.397	−2.430	−2.458
0.52	−1.439	−1.722	−1.880	−1.988	−2.067	−2.128	−2.178	−2.218	−2.251	−2.280
0.54	−1.275	−1.559	−1.717	−1.825	−1.904	−1.966	−2.015	−2.056	−2.090	−2.118
0.56	−1.120	−1.404	−1.563	−1.671	−1.751	−1.814	−1.864	−1.905	−1.939	−1.968
0.58	−0.979	−1.263	−1.423	−1.531	−1.612	−1.674	−1.725	−1.767	−1.801	−1.831
0.60	−0.848	−1.133	−1.293	−1.401	−1.482	−1.545	−1.596	−1.638	−1.673	−1.703
0.62	−0.729	−1.014	−1.174	−1.284	−1.365	−1.428	−1.479	−1.522	−1.557	−1.587
0.64	−0.622	−0.907	−1.067	−1.177	−1.258	−1.322	−1.373	−1.416	−1.452	−1.482
0.66	−0.519	−0.804	−0.965	−1.075	−1.156	−1.220	−1.272	−1.315	−1.351	−1.381
0.68	−0.425	−0.711	−0.872	−0.981	−1.063	−1.127	−1.179	−1.222	−1.259	−1.289
0.70	−0.334	−0.620	−0.781	−0.891	−0.973	−1.037	−1.090	−1.133	−1.169	−1.200
0.72	−0.249	−0.535	−0.696	−0.806	−0.888	−0.953	−1.005	−1.048	−1.085	−1.116
0.74	−0.171	−0.457	−0.618	−0.729	−0.811	−0.875	−0.928	−0.971	−1.008	−1.040
0.76	−0.0966	−0.383	−0.544	−0.655	−0.737	−0.802	−0.854	−0.898	−0.935	−0.967
0.78	−0.0366	−0.316	−0.478	−0.588	−0.671	−0.736	−0.789	−0.832	−0.870	−0.901
0.80	−0.0550	−0.252	−0.414	−0.524	−0.607	−0.672	−0.725	−0.769	−0.806	−0.838

$T_r \backslash P_r$	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.50	−2.481	−2.501	−2.517	−2.532	−2.544	−2.579	−2.587	−2.577	−2.555	−2.524	−2.487
0.52	−2.303	−2.324	−2.341	−2.356	−2.368	−2.406	−2.416	−2.408	−2.388	−2.360	−2.325
0.54	−2.142	−2.163	−2.180	−2.195	−2.208	−2.247	−2.259	−2.254	−2.237	−2.210	−2.178
0.56	−1.993	−2.014	−2.032	−2.048	−2.061	−2.103	−2.117	−2.114	−2.098	−2.075	−2.044
0.58	−1.856	−1.877	−1.896	−1.912	−1.925	−1.969	−1.985	−1.984	−1.971	−1.949	−1.921
0.60	−1.728	−1.750	−1.769	−1.785	−1.799	−1.845	−1.863	−1.864	−1.853	−1.833	−1.807
0.62	−1.613	−1.635	−1.654	−1.671	−1.685	−1.733	−1.753	−1.755	−1.746	−1.729	−1.705
0.64	−1.508	−1.530	−1.549	−1.567	−1.581	−1.631	−1.652	−1.657	−1.650	−1.634	−1.612
0.66	−1.408	−1.431	−1.450	−1.468	−1.483	−1.533	−1.557	−1.563	−1.558	−1.544	−1.523
0.68	−1.316	−1.339	−1.359	−1.377	−1.392	−1.444	−1.469	−1.477	−1.474	−1.461	−1.442
0.70	−1.227	−1.250	−1.271	−1.288	−1.304	−1.357	−1.384	−1.393	−1.391	−1.380	−1.363
0.72	−1.143	−1.167	−1.187	−1.205	−1.221	−1.276	−1.303	−1.314	−1.313	−1.304	−1.288
0.74	−1.067	−1.090	−1.111	−1.129	−1.145	−1.201	−1.230	−1.242	−1.242	−1.234	−1.220
0.76	−0.994	−1.018	−1.039	−1.057	−1.073	−1.130	−1.160	−1.173	−1.174	−1.167	−1.154
0.78	−0.929	−0.953	−0.974	−0.992	−1.009	−1.066	−1.097	−1.111	−1.113	−1.107	−1.095
0.80	−0.866	−0.890	−0.911	−0.930	−0.946	−1.005	−1.037	−1.052	−1.055	−1.050	−1.039

TABLE 3. VALUES OF LOG $\left(\frac{f_l}{P}\right)^{(1)}$

T_r \ P_r	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
0.50	−0.285	−2.834	−2.843	−2.852	−2.860	−2.869	−2.878	−2.886	−2.895	−2.904
0.52	−2.521	−2.529	−2.538	−2.546	−2.555	−2.564	−2.572	−2.580	−2.589	−2.597
0.54	−2.264	−2.273	−2.281	−2.290	−2.298	−2.307	−2.315	−2.323	−2.332	−2.340
0.56	−2.046	−2.054	−2.062	−2.071	−2.079	−2.087	−2.095	−2.103	−2.111	−2.119
0.58	−1.847	−1.855	−1.864	−1.872	−1.880	−1.888	−1.896	−1.903	−1.911	−1.919
0.60	−1.662	−1.670	−1.678	−1.686	−1.694	−1.702	−1.710	−1.717	−1.725	−1.733
0.62	−1.486	−1.494	−1.502	−1.510	−1.518	−1.525	−1.533	−1.540	−1.548	−1.555
0.64	−1.307	−1.315	−1.323	−1.331	−1.338	−1.346	−1.353	−1.360	−1.368	−1.375
0.66	−1.165	−1.173	−1.181	−1.188	−1.196	−1.203	−1.211	−1.218	−1.225	−1.232
0.68	−1.033	−1.041	−1.049	−1.056	−1.064	−1.071	−1.078	−1.085	−1.092	−1.099
0.70	−0.929	−0.937	−0.944	−0.952	−0.959	−0.966	−0.973	−0.980	−0.987	−0.994
0.72	−0.825	−0.833	−0.840	−0.847	−0.855	−0.862	−0.868	−0.875	−0.882	−0.888
0.74	−0.731	−0.738	−0.745	−0.752	−0.759	−0.766	−0.773	−0.780	−0.786	−0.793
0.76	−0.647	−0.654	−0.661	−0.668	−0.675	−0.682	−0.688	−0.695	−0.701	−0.708
0.78	−0.534	−0.561	−0.568	−0.575	−0.582	−0.589	−0.595	−0.602	−0.608	−0.614
0.80	−0.0246	−0.481	−0.488	−0.494	−0.501	−0.507	−0.514	−0.520	−0.527	−0.532

T_r \ P_r	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.50	−2.912	−2.921	−2.930	−2.938	−2.947	−2.990	−3.033	−3.076	−3.118	−3.161	−3.204
0.52	−2.606	−2.614	−2.623	−2.631	−2.639	−2.681	−2.723	−2.764	−2.805	−2.847	−2.888
0.54	−2.348	−2.357	−2.365	−2.373	−2.381	−2.422	−2.462	−2.502	−2.542	−2.581	−2.621
0.56	−2.127	−2.135	−2.143	−2.151	−2.159	−2.198	−2.236	−2.275	−2.313	−2.351	−2.389
0.58	−1.927	−1.935	−1.942	−1.950	−1.958	−1.995	−2.033	−2.070	−2.106	−2.143	−2.179
0.60	−1.740	−1.748	−1.755	−1.763	−1.770	−1.807	−1.842	−1.878	−1.913	−1.948	−1.983
0.62	−1.562	−1.570	−1.577	−1.584	−1.591	−1.627	−1.661	−1.695	−1.729	−1.762	−1.795
0.64	−1.382	−1.389	−1.399	−1.403	−1.411	−1.444	−1.478	−1.510	−1.542	−1.574	−1.605
0.66	−1.239	−1.246	−1.253	−1.260	−1.266	−1.299	−1.331	−1.362	−1.393	−1.423	−1.453
0.68	−1.105	−1.112	−1.119	−1.125	−1.132	−1.164	−1.194	−1.224	−1.251	−1.282	−1.310
0.70	−1.000	−1.007	−1.013	−1.020	−1.026	−1.056	−1.086	−1.114	−1.142	−1.169	−1.196
0.72	−0.895	−0.901	−0.908	−0.914	−0.920	−0.949	−0.977	−1.004	−1.031	−1.056	−1.082
0.74	−0.799	−0.805	−0.811	−0.817	−0.823	−0.852	−0.879	−0.904	−0.929	−0.954	−0.978
0.76	−0.714	−0.720	−0.726	−0.732	−0.737	−0.765	−0.791	−0.815	−0.839	−0.862	−0.885
0.78	−0.621	−0.626	−0.632	−0.638	−0.643	−0.670	−0.695	−0.719	−0.741	−0.763	−0.785
0.80	−0.539	−0.544	−0.550	−0.556	−0.561	−0.587	−0.611	−0.634	−0.656	−0.677	−0.697

the extended correlation. It is anticipated that this satisfactory result should also be reflected in the proposed evaluation of (f_l/P), Z_T and Z_P.

LIQUID PHASE FUGACITY COEFFICIENT

Calculation of the liquid phase fugacity coefficient (f_l/P) may begin with the quantity f_l^s. At equilibrium,

$$f_l^s = f_v^s \tag{1}$$

By definition

$$f_v^s = \phi_v^s P^s \tag{2}$$

The fugacity coefficient of saturated vapor is evaluated from the following equation:

$$\phi_v^s = \exp\left[\int_0^{P_r^s} \frac{Z_v - 1}{P_r}\, dP_r\right] \tag{3}$$

with the condition that $f/P \rightarrow 1$ as $P \rightarrow 0$. Since the gas phase exists only in the very low P_r region, Z values obtained from the second virial coefficient are adequate for representing the data. Therefore

$$\phi_v^s = \exp\left(\frac{\beta_r P_r^s}{T_r}\right) \tag{4}$$

where $\beta_r = \beta P_c/RT_c$ is the reduced second virial coefficient. The values of β_r were obtained from the generalized second virial coefficients reported earlier (Chang and Lu, 1972).

The pressure effect on liquid fugacity is given by

$$\left(\frac{\partial \ln f_l}{\partial P}\right)_T = \frac{Z_l}{P} \tag{5}$$

Integrating from the saturation pressure P^s to P, and substituting $\phi_v^s P^s$ for the saturated liquid fugacity gives

$$\ln\frac{f_l}{P} = \ln\frac{\phi_v^s P_r^s}{P_r} + \int_{P_r^s}^{P_r} \frac{Z_l}{P_r}\, dP_r \tag{6}$$

In this calculation, values of vapor pressure P^s and Z_l are required. Vapor pressures of normal paraffin hydrocarbons contained in the American Petroleum Institute Project 44 tables were used by Chao et al. (1971). Carruth and Kobayashi (1972) used instead their recently measured vapor pressures of the homologous series ethane through n-decane and reported that some differences were noted between their work and that of Chao et al., mostly in the resulting log $(f_l/P)^{(1)}$ function, probably due to different input data. In this investigation, an effort was made to correlate vapor pressures of both hydrocarbons and nonhydrocarbons, using the values of argon, methane, oxygen, nitrogen, benzene and n-heptane, compiled by Rowlinson (1969), according to the following equation originally proposed by Pitzer et al. (1965).

$$\log P_r^s = \log P_r^{s(0)} + \omega \log P_r^{s(1)} \tag{7}$$

TABLE 4. VALUES OF $Z_p^{(0)}$

T_r \ P_r	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
0.50	0.0001	0.0004	0.0008	0.0013	0.0019	0.0025	0.0032	0.0039	0.0046	0.0053
0.52	0.0001	0.0003	0.0006	0.0010	0.0015	0.0021	0.0027	0.0033	0.0039	0.0046
0.54	0.0001	0.0002	0.0005	0.0008	0.0013	0.0017	0.0023	0.0029	0.0036	0.0043
0.56	0.0000	0.0002	0.0004	0.0007	0.0011	0.0016	0.0022	0.0028	0.0035	0.0042
0.58	0.0000	0.0002	0.0004	0.0008	0.0012	0.0017	0.0023	0.0030	0.0037	0.0045
0.60	0.0000	0.0002	0.0005	0.0009	0.0014	0.0020	0.0027	0.0035	0.0043	0.0053
0.62	0.0001	0.0003	0.0007	0.0011	0.0017	0.0024	0.0032	0.0042	0.0052	0.0063
0.64	0.0001	0.0003	0.0008	0.0013	0.0021	0.0029	0.0038	0.0049	0.0060	0.0073
0.66	0.0001	0.0004	0.0009	0.0016	0.0025	0.0034	0.0044	0.0057	0.0070	0.0085
0.68	0.0001	0.0005	0.0011	0.0019	0.0029	0.0040	0.0052	0.0066	0.0081	0.0098
0.70	0.0002	0.0006	0.0013	0.0022	0.0033	0.0045	0.0060	0.0077	0.0093	0.0112
0.72	0.0002	0.0007	0.0015	0.0025	0.0038	0.0054	0.0069	0.0087	0.0106	0.0126
0.74	0.0002	0.0008	0.0017	0.0029	0.0043	0.0060	0.0079	0.0098	0.0119	0.0140
0.76	0.0002	0.0009	0.0019	0.0032	0.0048	0.0066	0.0086	0.0108	0.0131	0.0155
0.78	0.0003	0.0010	0.0021	0.0035	0.0053	0.0073	0.0095	0.0120	0.0145	0.0171
0.80		0.0010	0.0023	0.0039	0.0058	0.0085	0.0109	0.0134	0.0160	0.0186

T_r \ P_r	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.50	0.0060	0.0068	0.0075	0.0082	0.0089	0.0123	0.0157	0.0188	0.0215	0.0239	0.0255
0.52	0.0054	0.0061	0.0069	0.0077	0.0085	0.0122	0.0161	0.0198	0.0233	0.0262	0.0290
0.54	0.0050	0.0058	0.0066	0.0075	0.0084	0.0126	0.0172	0.0215	0.0255	0.0292	0.0326
0.56	0.0050	0.0058	0.0067	0.0077	0.0087	0.0137	0.0188	0.0238	0.0285	0.0328	0.0368
0.58	0.0055	0.0063	0.0073	0.0084	0.0096	0.0155	0.0212	0.0268	0.0320	0.0368	0.0415
0.60	0.0063	0.0073	0.0085	0.0097	0.0110	0.0175	0.0239	0.0299	0.0356	0.0413	0.0466
0.62	0.0074	0.0086	0.0099	0.0112	0.0125	0.0200	0.0269	0.0335	0.0398	0.0460	0.0520
0.64	0.0086	0.0100	0.0115	0.0128	0.0144	0.0225	0.0302	0.0375	0.0445	0.0512	0.0576
0.66	0.0100	0.0115	0.0131	0.0148	0.0165	0.0253	0.0337	0.0414	0.0489	0.0562	0.0633
0.68	0.0115	0.0132	0.0150	0.0168	0.0187	0.0282	0.0372	0.0455	0.0535	0.0615	0.0695
0.70	0.0130	0.0150	0.0170	0.0190	0.0210	0.0314	0.0409	0.0497	0.0586	0.0674	0.0756
0.72	0.0148	0.0169	0.0190	0.0211	0.0233	0.0341	0.0445	0.0541	0.0636	0.0730	0.0822
0.74	0.0162	0.0185	0.0208	0.0231	0.0255	0.0372	0.0481	0.0585	0.0689	0.0790	0.0892
0.76	0.0180	0.0204	0.0228	0.0253	0.0278	0.0403	0.0520	0.0630	0.0740	0.0850	0.0958
0.78	0.0197	0.0223	0.0250	0.0275	0.0301	0.0432	0.0559	0.0677	0.0794	0.0907	0.1016
0.80	0.0214	0.0241	0.0269	0.0296	0.0325	0.0464	0.0596	0.0724	0.0848	0.0966	0.1081

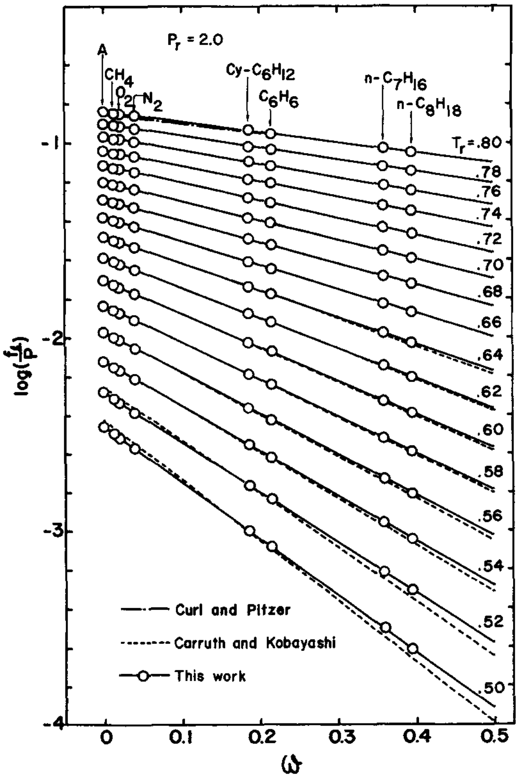

Fig. 1. Dependence of log (f_l/P) upon acentric factor at P_r = 2.0.

These vapor pressure values were used in the development of the extended Pitzer's correlation of Z. The values obtained for log $P_r^{s(0)}$ and log $P_r^{s(1)}$ are presented in Table 1, with the values reported by Pitzer et al. (1955) and Carruth and Kobayashi (1972) included for comparison. The satisfactory agreement is obvious.

Values of Z_l were calculated from the previous correlation (Lu et al., 1973) for 8 compounds, including cyclohexane, *n*-octane, and the 6 compounds mentioned above. *n*-octane was added because of its high acentric factor value (ω = 0.395), and cyclohexane was chosen because it is a cyclic organic compound.

Values of (f/P) were then calculated at regular intervals of T_r and P_r in the $0.5 \leq T_r \leq 0.8$ and $0.2 \leq P_r \leq 9.0$ region, using the values of P_r^s and Z_l obtained above by means of Equation (6). The resulting f_l/P values were then correlated by means of Equation (8).

$$\log \frac{f_l}{P} = \left[\log\left(\frac{f_l}{P}\right)\right]^{(0)} + \omega\left[\log\left(\frac{f_l}{P}\right)\right]^{(1)} \qquad (8)$$

A linear regression technique was employed to obtain the values of $[\log(f_l/P)]^{(0)}$ and $[\log(f_l/P)]^{(1)}$, which are presented at selected intervals of T_r and P_r in Tables 2 and 3.

The dependence of log (f/P) upon ω is illustrated in Figure 1 at P_r = 2.0 for 16 T_r values. The results of Curl and Pitzer (1958) and Carruth and Kobayashi (1972) at the same P_r and T_r conditions are also included in this figure for comparison. The dependence of $[\log(f_l/P)]^{(0)}$

and that of $[\log(f_l/P)]^{(1)}$ upon T_r and P_r are depicted in Figures 2 and 3 respectively. In these figures, the values of Curl and Pitzer (1958), Chao et al. (1971), and Carruth and Kobayashi (1972) are also included for comparison. The calculated values agree well with those of Curl and Pitzer at $T_r = 0.8$, which is the lower limit of their correlation, and those of Carruth and Kobayashi in the $0.54 \leq T_r \leq 0.64$ region. The values obtained in this investigation are somewhat smoother than those reported by Chao et al. at T_r from 0.50 to 0.70. Although some discrepancies are observed between this work and the values of Chao et al. and Carruth and Kobayashi at $T_r = 0.52$ and $T_r = 0.50$, particularly for the $[\log(f_l/P)]^{(1)}$ values, the difference in the final values of f_l/P is not significant.

DERIVATIVE COMPRESSIBILITY FACTORS, Z_P AND Z_T

Numerous thermodynamic properties involve the partial derivatives of volume with respect to T or P, namely

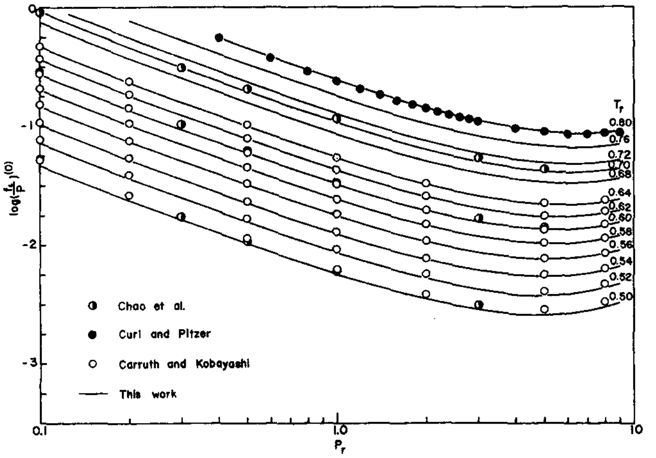

Fig. 2. Effect of P_r anl T_r on $\log(f_l/P)^{(0)}$.

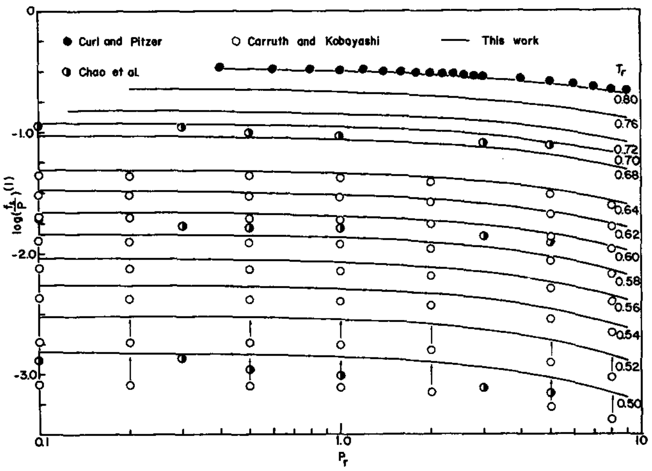

Fig. 3. Effect of P_r and T_r on $\log(f_l/P)^{(1)}$.

TABLE 5. VALUES OF $Z_p^{(1)}$

T_r \ P_r	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
0.50	−0.0006	−0.0008	−0.0011	−0.0013	−0.0015	−0.0017	−0.0020	−0.0021	−0.0023	−0.0025
0.52	−0.0005	−0.0009	−0.0013	−0.0016	−0.0020	−0.0023	−0.0025	−0.0028	−0.0031	−0.0035
0.54	−0.0005	−0.0010	−0.0014	−0.0019	−0.0024	−0.0029	−0.0033	−0.0038	−0.0042	−0.0046
0.56	−0.0004	−0.0010	−0.0017	−0.0023	−0.0029	−0.0036	−0.0041	−0.0048	−0.0055	−0.0060
0.58	−0.0004	−0.0011	−0.0018	−0.0026	−0.0034	−0.0043	−0.0050	−0.0060	−0.0068	−0.0077
0.60	−0.0004	−0.0011	−0.0020	−0.0029	−0.0039	−0.0050	−0.0061	−0.0073	−0.0085	−0.0096
0.62	−0.0004	−0.0011	−0.0022	−0.0033	−0.0045	−0.0058	−0.0075	−0.0089	−0.0104	−0.0119
0.64	−0.0003	−0.0012	−0.0024	−0.0037	−0.0051	−0.0067	−0.0085	−0.0101	−0.0120	−0.0138
0.66	−0.0003	−0.0013	−0.0026	−0.0040	−0.0057	−0.0076	−0.0095	−0.0115	−0.0136	−0.0159
0.68	−0.0003	−0.0014	−0.0028	−0.0044	−0.0064	−0.0085	−0.0108	−0.0130	−0.0155	−0.0180
0.70	−0.0002	−0.0014	−0.0030	−0.0049	−0.0072	−0.0096	−0.0124	−0.0150	−0.0178	−0.0205
0.72	−0.0002	−0.0015	−0.0031	−0.0053	−0.0079	−0.0107	−0.0138	−0.0168	−0.0198	−0.0228
0.74	−0.0002	−0.0015	−0.0033	−0.0057	−0.0085	−0.0115	−0.0146	−0.0179	−0.0213	−0.0249
0.76	−0.0001	−0.0015	−0.0034	−0.0060	−0.0090	−0.0123	−0.0155	−0.0190	−0.0227	−0.0265
0.78	−0.0001	−0.0016	−0.0036	−0.0063	−0.0094	−0.0128	−0.0165	−0.0202	−0.0241	−0.0281
0.80		−0.0016	−0.0037	−0.0065	−0.0098	−0.0134	−0.0171	−0.0212	−0.0253	−0.0294

T_r \ P_r	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.50	−0.0026	−0.0027	−0.0029	−0.0030	−0.0031	−0.0039	−0.0045	−0.0051	−0.0058	−0.0064	−0.0070
0.52	−0.0037	−0.0040	−0.0044	−0.0047	−0.0050	−0.0065	−0.0080	−0.0095	−0.0110	−0.0126	−0.0142
0.54	−0.0051	−0.0055	−0.0060	−0.0065	−0.0070	−0.0093	−0.0117	−0.0140	−0.0164	−0.0189	−0.0215
0.56	−0.0068	−0.0075	−0.0081	−0.0088	−0.0095	−0.0130	−0.0165	−0.0198	−0.0230	−0.0261	−0.0292
0.58	−0.0086	−0.0095	−0.0105	−0.0115	−0.0124	−0.0170	−0.0214	−0.0255	−0.0295	−0.0332	−0.0367
0.60	−0.0108	−0.0120	−0.0132	−0.0144	−0.0155	−0.0213	−0.0265	−0.0315	−0.0360	−0.0402	−0.0439
0.62	−0.0134	−0.0149	−0.0163	−0.0178	−0.0191	−0.0260	−0.0322	−0.0376	−0.0426	−0.0472	−0.0511
0.64	−0.0156	−0.0175	−0.0192	−0.0210	−0.0227	−0.0309	−0.0380	−0.0441	−0.0495	−0.0540	−0.0578
0.66	−0.0180	−0.0204	−0.0225	−0.0246	−0.0266	−0.0362	−0.0441	−0.0510	−0.0565	−0.0609	−0.0648
0.68	−0.0205	−0.0230	−0.0256	−0.0280	−0.0305	−0.0415	−0.0500	−0.0567	−0.0623	−0.0670	−0.0707
0.70	−0.0232	−0.0260	−0.0290	−0.0316	−0.0342	−0.0460	−0.0555	−0.0629	−0.0686	−0.0731	−0.0765
0.72	−0.0259	−0.0290	−0.0320	−0.0350	−0.0380	−0.0515	−0.0613	−0.0683	−0.0740	−0.0784	−0.0817
0.74	−0.0283	−0.0316	−0.0350	−0.0385	−0.0416	−0.0563	−0.0664	−0.0740	−0.0796	−0.0838	−0.0870
0.76	−0.0305	−0.0342	−0.0379	−0.0414	−0.0448	−0.0605	−0.0715	−0.0796	−0.0852	−0.0893	−0.0924
0.78	−0.0322	−0.0362	−0.0402	−0.0440	−0.0477	−0.0644	−0.0765	−0.0846	−0.0901	−0.0939	−0.0970
0.80	−0.0335	−0.0375	−0.0418	−0.0460	−0.0501	−0.0681	−0.0813	−0.0897	−0.0951	−0.0988	−0.1013

TABLE 6. VALUES OF $Z_T^{(0)}$

$T_r \backslash P_r$	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
0.50	0.0130	0.0236	0.0349	0.0460	0.0564	0.0678	0.0788	0.0890	0.1000	0.1110
0.52	0.0138	0.0252	0.0373	0.0492	0.0602	0.0720	0.0835	0.0941	0.1053	0.1166
0.54	0.0143	0.0269	0.0398	0.0523	0.0640	0.0761	0.0882	0.0992	0.1107	0.1221
0.56	0.0150	0.0286	0.0420	0.0554	0.0679	0.0803	0.0929	0.1043	0.1161	0.1278
0.58	0.0158	0.0302	0.0445	0.0585	0.0718	0.0846	0.0976	0.1094	0.1215	0.1334
0.60	0.0162	0.0320	0.0468	0.0616	0.0753	0.0888	0.1023	0.1145	0.1270	0.1390
0.62	0.0170	0.0338	0.0493	0.0647	0.0794	0.0932	0.1069	0.1197	0.1325	0.1445
0.64	0.0177	0.0356	0.0518	0.0679	0.0831	0.0975	0.1116	0.1248	0.1379	0.1500
0.66	0.0181	0.0372	0.0540	0.0708	0.0869	0.1017	0.1163	0.1299	0.1433	0.1558
0.68	0.0190	0.0389	0.0564	0.0739	0.0907	0.1059	0.1210	0.1350	0.1487	0.1614
0.70	0.0199	0.0405	0.0589	0.0770	0.0945	0.1100	0.1257	0.1400	0.1541	0.1668
0.72	0.0203	0.0422	0.0614	0.0800	0.0982	0.1142	0.1303	0.1451	0.1597	0.1724
0.74	0.0210	0.0440	0.0638	0.0831	0.1021	0.1185	0.1350	0.1500	0.1650	0.1780
0.76	0.0219	0.0458	0.0661	0.0861	0.1060	0.1227	0.1398	0.1551	0.1703	0.1838
0.78	0.0225	0.0474	0.0685	0.0892	0.1098	0.1269	0.1444	0.1602	0.1758	0.1893
0.80		0.0492	0.0712	0.0923	0.1137	0.1311	0.1491	0.1653	0.1812	0.1950

$T_r \backslash P_r$	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.50	0.1217	0.1326	0.1439	0.1574	0.1704	0.2180	0.2569	0.2893	0.3195	0.3471	0.3715
0.52	0.1273	0.1384	0.1492	0.1622	0.1750	0.2212	0.2581	0.2887	0.3166	0.3423	0.3647
0.54	0.1332	0.1440	0.1547	0.1672	0.1796	0.2242	0.2595	0.2882	0.3140	0.3378	0.3580
0.56	0.1390	0.1498	0.1601	0.1721	0.1840	0.2273	0.2606	0.2878	0.3115	0.3332	0.3513
0.58	0.1446	0.1554	0.1655	0.1769	0.1884	0.2302	0.2620	0.2873	0.3087	0.3285	0.3447
0.60	0.1502	0.1610	0.1708	0.1820	0.1930	0.2333	0.2632	0.2868	0.3061	0.3240	0.3380
0.62	0.1560	0.1667	0.1762	0.1868	0.1974	0.2364	0.2644	0.2862	0.3035	0.3194	0.3315
0.64	0.1618	0.1722	0.1817	0.1919	0.2020	0.2395	0.2658	0.2858	0.3009	0.3146	0.3247
0.66	0.1675	0.1779	0.1870	0.1967	0.2063	0.2423	0.2670	0.2855	0.2983	0.3099	0.3180
0.68	0.1731	0.1834	0.1925	0.2019	0.2108	0.2454	0.2683	0.2849	0.2959	0.3053	0.3115
0.70	0.1790	0.1890	0.1979	0.2067	0.2154	0.2483	0.2696	0.2844	0.2932	0.3005	0.3047
0.72	0.1845	0.1947	0.2032	0.2119	0.2199	0.2513	0.2708	0.2840	0.2905	0.2959	0.2980
0.74	0.1902	0.2003	0.2085	0.2168	0.2241	0.2543	0.2722	0.2837	0.2880	0.2913	0.2914
0.76	0.1960	0.2059	0.2139	0.2220	0.2285	0.2574	0.2735	0.2832	0.2857	0.2864	0.2846
0.78	0.2018	0.2117	0.2194	0.2268	0.2330	0.2604	0.2747	0.2828	0.2828	0.2818	0.2779
0.80	0.2075	0.2172	0.2247	0.2319	0.2375	0.2635	0.2760	0.2822	0.2804	0.2772	0.2713

$(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$. Reid and Valbert (1962) first introduced the concept of the derivative compressibility factors Z_P and Z_T for obtaining these partial derivatives. The quantities Z_P and Z_T are defined by Equations (9) and (10), respectively.

$$Z_P = Z - P_r \left(\frac{\partial Z}{\partial P_r}\right)_{T_r} \tag{9}$$

$$Z_T = Z + T_r \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \tag{10}$$

They can be further expressed linearly in terms of ω as follows:

$$Z_P = Z_P^{(0)} + \omega\, Z_P^{(1)} \tag{11}$$

$$Z_T = Z_T^{(0)} + \omega\, Z_T^{(1)} \tag{12}$$

where

$$Z_P^{(0)} = Z^{(0)} - P_r \left(\frac{\partial Z^{(0)}}{\partial P_r}\right)_{T_r} \tag{13}$$

$$Z_P^{(1)} = Z^{(1)} - P_r \left(\frac{\partial Z^{(1)}}{\partial P_r}\right)_{T_r} \tag{14}$$

$$Z_T^{(0)} = Z^{(0)} + T_r \left(\frac{\partial Z^{(0)}}{\partial T_r}\right)_{P_r} \tag{15}$$

and

$$Z_T^{(1)} = Z^{(1)} + T_r \left(\frac{\partial Z^{(1)}}{\partial T_r}\right)_{P_r} \tag{16}$$

The $Z^{(0)}$ and $Z^{(1)}$ values reported previously have been used in these expressions for the determination of Z_P and Z_T from Equations (11) and (12). However, the $Z_P^{(0)}$ and $Z_P^{(1)}$ values obtained from Equations (13) and (14) were found to be unsatisfactory. Excessive scatter in these values may be attributed to the relatively small values of Z_P in comparison with the values of Z and $P_r \left(\frac{\partial Z}{\partial P_r}\right)_{T_r}$. For this reason, Equations (9) and (10) are rearranged as follows:

$$Z_P = -P_r^2 \left[\frac{\partial (Z/P_r)}{\partial P_r}\right]_{T_r} \tag{17}$$

$$Z_T = \left[\frac{\partial (ZT_r)}{\partial T_r}\right]_{P_r} \tag{18}$$

These two equations are the working equations for evaluating Z_P and Z_T in this investigation. In the evaluation, both graphical and numerical techniques were employed. The quantities Z/P_r and ZT_r were first fitted by means of a suitable polynomial, and then partial derivatives were evaluated by Equations (17) and (18). Even though the polynomial equation seems to adequately represent the data as a whole, uncertainties in the slopes are often observed. For this reason, the derivatives were also evaluated by a graphical procedure. The smoothed and final results were obtained by using both sets of values through a cross-plotting procedure. Values of $Z_P^{(0)}$,

TABLE 7. VALUES OF $Z_T^{(1)}$

$T_r \backslash P_r$	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
0.50	−0.0070	−0.0159	−0.0244	−0.0319	−0.0390	−0.0448	−0.0496	−0.0534	−0.0559	−0.0565
0.52	−0.0068	−0.0156	−0.0240	−0.0314	−0.0383	−0.0439	−0.0486	−0.0519	−0.0539	−0.0539
0.54	−0.0066	−0.0153	−0.0237	−0.0309	−0.0378	−0.0431	−0.0476	−0.0504	−0.0520	−0.0513
0.56	−0.0064	−0.0150	−0.0233	−0.0304	−0.0371	−0.0423	−0.0466	−0.0490	−0.0500	−0.0487
0.58	−0.0061	−0.0148	−0.0229	−0.0299	−0.0365	−0.0416	−0.0455	−0.0477	−0.0480	−0.0461
0.60	−0.0059	−0.0145	−0.0226	−0.0294	−0.0359	−0.0408	−0.0444	−0.0462	−0.0460	−0.0436
0.62	−0.0057	−0.0143	−0.0222	−0.0289	−0.0353	−0.0400	−0.0433	−0.0449	−0.0440	−0.0411
0.64	−0.0054	−0.0140	−0.0219	−0.0285	−0.0347	−0.0392	−0.0423	−0.0433	−0.0420	−0.0385
0.66	−0.0052	−0.0138	−0.0215	−0.0280	−0.0341	−0.0384	−0.0413	−0.0419	−0.0400	−0.0360
0.68	−0.0050	−0.0136	−0.0211	−0.0275	−0.0334	−0.0376	−0.0402	−0.0405	−0.0381	−0.0334
0.70	−0.0049	−0.0133	−0.0208	−0.0270	−0.0329	−0.0368	−0.0392	−0.0390	−0.0361	−0.0309
0.72	−0.0048	−0.0130	−0.0204	−0.0266	−0.0322	−0.0360	−0.0381	−0.0376	−0.0342	−0.0283
0.74	−0.0046	−0.0128	−0.0201	−0.0261	−0.0316	−0.0352	−0.0371	−0.0362	−0.0322	−0.0258
0.76	−0.0042	−0.0126	−0.0198	−0.0257	−0.0310	−0.0344	−0.0361	−0.0348	−0.0302	−0.0232
0.78	−0.0040	−0.0123	−0.0194	−0.0252	−0.0304	−0.0336	−0.0350	−0.0334	−0.0283	−0.0206
0.80		−0.0120	−0.0190	−0.0248	−0.0298	−0.0329	−0.0340	−0.0320	−0.0263	−0.0180

$T_r \backslash P_r$	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.50	−0.0550	−0.0535	−0.0508	−0.0475	−0.0438	−0.026	−0.005	+0.018	+0.044	+0.072	+0.100
0.52	−0.0518	−0.0494	−0.0460	−0.0420	−0.0371	−0.015	+0.012	+0.040	+0.072	+0.105	+0.139
0.54	−0.0485	−0.0454	−0.0412	−0.0363	−0.0306	−0.003	+0.029	+0.063	+0.100	+0.138	+0.177
0.56	−0.0454	−0.0414	−0.0365	−0.0307	−0.0240	+0.009	+0.046	+0.085	+0.127	+0.171	+0.215
0.58	−0.0421	−0.0375	−0.0317	−0.0251	−0.0174	+0.020	+0.063	+0.108	+0.155	+0.205	+0.253
0.60	−0.0390	−0.0335	−0.0269	−0.0196	−0.0109	+0.032	+0.080	+0.130	+0.183	+0.237	+0.290
0.62	−0.0358	−0.0296	−0.0220	−0.0140	−0.0041	+0.044	+0.097	+0.152	+0.210	+0.270	+0.330
0.64	−0.0326	−0.0256	−0.0174	−0.0083	+0.0024	+0.055	+0.114	+0.175	+0.238	+0.304	+0.368
0.66	−0.0294	−0.0216	−0.0126	−0.0027	+0.0090	+0.067	+0.130	+0.197	+0.266	+0.337	+0.405
0.68	−0.0262	−0.0177	−0.0078	+0.0029	+0.0156	+0.079	+0.148	+0.219	+0.294	+0.370	+0.444
0.70	−0.0230	−0.0137	−0.0029	+0.0085	+0.0222	+0.090	+0.165	+0.241	+0.321	+0.404	+0.482
0.72	−0.0199	−0.0098	+0.0019	+0.0141	+0.0289	+0.102	+0.181	+0.264	+0.349	+0.437	+0.520
0.74	−0.0167	−0.0058	+0.0067	+0.0198	+0.0354	+0.114	+0.198	+0.286	+0.376	+0.470	+0.558
0.76	−0.0134	−0.0018	+0.0115	+0.0252	+0.0420	+0.126	+0.215	+0.309	+0.404	+0.503	+0.595
0.78	−0.0102	+0.0022	+0.0162	+0.0310	+0.0487	+0.138	+0.232	+0.331	+0.432	+0.536	+0.633
0.80	−0.0070	+0.0062	+0.0212	+0.0368	+0.0553	+0.150	+0.249	+0.353	+0.460	+0.570	+0.672

$Z_P^{(1)}$, $Z_T^{(0)}$ and $Z_T^{(1)}$ are presented at selected intervals of T_r and P_r in Tables 4 to 7. The quantity $Z_P^{(0)}$ as a function of P_r at constant values of T_r and the quantity $Z_T^{(0)}$ as a function of T_r at constant values of P_r are depicted in Figures 4 and 5, respectively.

The usefulness of the derivative compressibility factors has been thoroughly discussed by Reid (Reid and Valbert, 1962; Reid and Sherwood, 1966). However, for the purpose of establishing the reliability of the Z_P and Z_T values obtained in this investigation for engineering calculations, values of $\frac{H^* - H}{T_c}$, $\left(\frac{\partial V}{\partial P}\right)_T$, and $\left(\frac{\partial V}{\partial T}\right)_P$ have been calculated for some arbitrarily chosen compounds at some arbitrarily chosen conditions and compared with the available literature values.

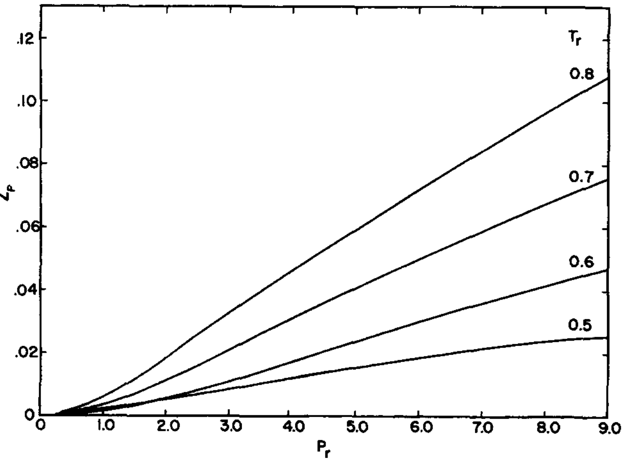

Fig. 4. Effect of P_r and T_r on $Z_P^{(0)}$.

The enthalpy departure from ideal gas $\frac{H^* - H}{T_c}$ has been calculated for liquid methane at $T_r = 0.8$ from the established Z and Z_T tables. In the calculation, second virial coefficients were used for the gas region and the enthalpy of vaporization was taken from the correlation of Pitzer et al. (1955). The pressure effect on the enthalpy of subcooled liquid is given by (Reid and Valbert, 1962)

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{RT}{P}(Z - Z_T) \qquad (19)$$

Integrating from saturated reduced pressure to P_r at constant T_r gives

$$\frac{H_l^s - H}{T_c} = -RT_r \int_{P_r^s}^{P_r} \frac{Z - Z_T}{P_r} dP_r$$

Therefore

$$\frac{H^* - H}{T_c} = \frac{H^* - H_v^s}{T_c} + \frac{\Delta H_{\text{vap}}}{T_c} + \frac{H_l^s - H}{T_c}$$

where

$$\Delta H_{\text{vap}} = H_v^s - H_l^s$$

and

$$\frac{H^* - H_v^s}{T_c} = RT_r^2 \int_0^{P_r^s} \left(\frac{1}{P_r}\right)\left(\frac{\partial Z_v}{\partial T_r}\right) dP_r$$

$$= RT_r^2 \int_0^{P_r^s} \left[-\frac{\beta_r}{T_r^2} + \frac{1}{T_r}\left(\frac{\partial \beta_r}{\partial T_r}\right)\right] dP_r \quad (20)$$

The calculated results are shown in Figure 6 together with those obtained from Pitzer's original table (Curl and Pitzer, 1958) and Yen and Alexander (1965). In addition, the calculated results of Lee and Edmister (1971) for liquid methane at $T_r = 0.815$ (−180°F) and the experimental data reported by Jones, Jr. et al. (1963) are also included for comparison. Although the values obtained in this investigation differ from two of the correlations, they do agree very satisfactorily with the experimental observations.

The partial derivatives $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ are evaluated by means of the following relationships (Reid and Valbert, 1962):

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{RZ_T}{P} \quad (21)$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RTZ_P}{P^2} \quad (22)$$

The calculated values of $(\partial V/\partial T)_P$ for carbon dioxide, *n*-heptane and *n*-octane, and the calculated values of $(\partial V/\partial P)_T$ for *n*-butane, cyclohexane and carbon dioxide are compared with the derived literature values in Tables 8 and 9, respectively. For carbon dioxide, $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ values were calculated from the values of $1/V\ (\partial V/\partial T)_P$ and $1/V\ (\partial V/\partial P)_T$, respectively, reported by Jenkin (1920). For all the other compounds, the partial derivatives were determined directly from the reported volumetric data by a graphical procedure. The apparent discrepancies may be partly due to the uncertainties involved in the graphical determination and partly due to the precision of the volumetric measurements and the reported significant figures of the data in the literature. In the last two tables, the largest differences occurred in the values for carbon dioxide, for which the two worst cases are considered here. At 34 atm and $T_r = 0.799$, the predicted $(\partial V/\partial T)_P$ value for carbon dioxide is 0.129 while the calculated literature value is 0.17. The difference in terms of Z_T is 0.017. At 81.6 atm and $T_r = 0.799$ the predicted $(\partial V/\partial P)_T$ value for carbon dioxide is −0.0141, while the calculated literature value is −0.011, representing a difference of 0.001 in the value of Z_P. However, the trend and the order of magnitude of the

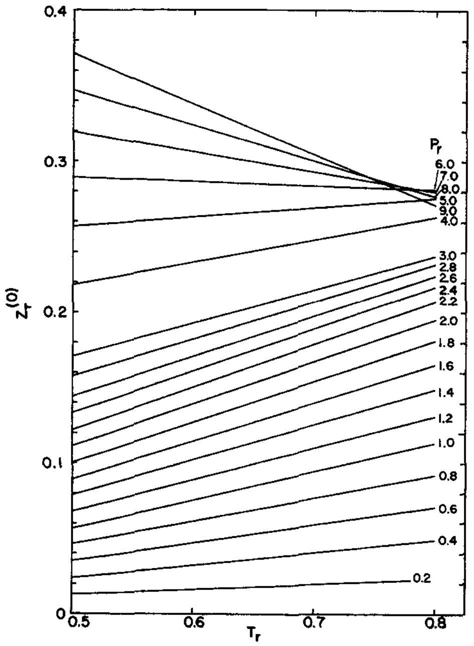

Fig. 5. Effect of P_r and T_r on $Z_T^{(0)}$.

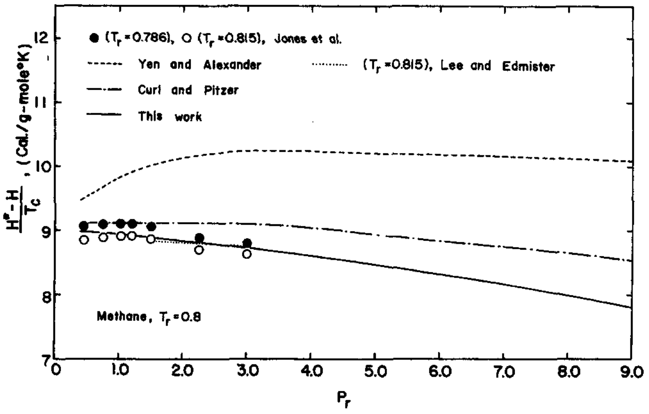

Fig. 6. Comparison of predicted and literature values of $\frac{H^* - H}{T_c}$ for liquid methane at $T_r = 0.8$.

TABLE 8. COMPARISON OF PREDICTED AND LITERATURE VALUES OF $(\partial V/\partial T)_P$

Compound	*P* atm	T_r	Literature	Predicted	Reference
Carbon dioxide	34.0	0.799	0.17 $\left[\frac{\text{cc/g-mol}}{°\text{K}}\right]$	0.129	Jenkin, 1920
	54.4		0.16	0.123	
	68.0		0.15	0.121	
	81.6		0.15	0.118	
n-heptane	98.7	0.506	0.13	0.160	Dolittle, 1963
		0.561	0.16	0.177	
		0.598	0.18	0.187	
		0.691	0.22	0.215	
		0.783	0.26	0.242	
n-octane	100	0.655	0.22	0.219	Felsing and Watson, 1942
		0.699	0.24	0.233	
		0.743	0.25	0.249	
		0.787	0.26	0.263	

TABLE 9. COMPARISON OF PREDICTED AND LITERATURE VALUES OF $\left(\frac{\partial V}{\partial P}\right)_T$

Compound	P atm	T_r	Literature	Predicted	Reference
n-butane	13.6	0.731	-4.4×10^{-5} $\left[\frac{\text{ft}^3\text{/lb.-mole}}{\text{lb./sq.in.abs.}}\right]$	-5.93×10^{-5}	Olds et al., 1944
	40.8		-4.1×10^{-5}	-4.81×10^{-5}	
	68.0		-3.5×10^{-5}	-4.39×10^{-5}	
	102.0		-2.9×10^{-5}	-3.77×10^{-5}	
	136.1		-2.8×10^{-5}	-3.26×10^{-5}	
	170.1		-2.5×10^{-5}	-2.84×10^{-5}	
	204.1		-2.2×10^{-5}	-2.49×10^{-5}	
	238.1		-2.0×10^{-5}	-2.21×10^{-5}	
Cyclohexane	68.0	0.562	-1.5×10^{-5} $\left[\frac{\text{ft}^3\text{/lb.-mole}}{\text{lb./sq.in.abs.}}\right]$	-1.33×10^{-5}	Reamer and Sage, 1957
	102.0		-1.5×10^{-5}	-1.26×10^{-5}	
	136.1		-1.4×10^{-5}	-1.26×10^{-5}	
	170.1		-1.3×10^{-5}	-1.16×10^{-5}	
	204.1		-1.2×10^{-5}	-1.05×10^{-5}	
	238.1		-1.2×10^{-5}	-0.95×10^{-5}	
	272.1		-1.1×10^{-5}	-0.86×10^{-5}	
	306.1		-1.0×10^{-5}	-0.78×10^{-5}	
Carbon dioxide	40.8	0.799	-1.3×10^{-2} $\left[\frac{\text{cc/g-mole}}{\text{atm}}\right]$	-1.56×10^{-2}	Jenkin, 1920
	54.4		-1.3×10^{-2}	-1.47×10^{-2}	
	68.0		-1.2×10^{-2}	-1.38×10^{-2}	
	81.6		-1.1×10^{-2}	-1.41×10^{-2}	

predicted values agree completely with the derived literature values. It should also be mentioned that Jenkin (1920) reported the values of $1/V\ (\partial V/\partial T)_P$ and $1/V\ (\partial V/\partial P)_T$ only to two significant figures and suggested that very slight alterations in the curves produced large changes in their slopes so that no great accuracy could be claimed for his tabulated figures.

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NOTATION

f = fugacity
H = enthalpy
P = pressure
R = gas constant
T = temperature
V = molal volume
Z = compressibility factor, $= PV/RT$
$Z^{(0)}$ = compressibility factor: for simple fluid
$Z^{(1)} = (\partial Z/\partial \omega)_{P_r,T_r}$
$Z_P = Z - P_r(\partial Z/\partial P_r)_{T_r}$
$Z_P{}^{(0)} = Z^{(0)} - P_r(\partial Z^{(0)}/\partial P_r)_{T_r}$
$Z_P{}^{(1)} = Z^{(1)} - P_r(\partial Z^{(1)}/\partial P_r)_{T_r}$
$Z_T = Z + T_r(\partial Z/\partial T_r)_{P_r}$
$Z_T{}^{(0)} = Z^{(0)} + T_r(\partial Z^{(0)}/\partial T_r)_{P_r}$
$Z_T{}^{(1)} = Z^{(1)} + T_r\ (\partial Z^{(1)}/\partial T_r)_{P_r}$
β = second virial coefficient
ϕ = fugacity coefficient
ω = acentric factor

Superscripts

$*$ = ideal gas state
s = saturation

Subscripts

c = critical state
l = liquid
v = vapor or gas
r = reduced quantity

LITERATURE CITED

Carruth, G. F., and R. Kobayashi, "Extension to Low Reduced Temperatures of Three-Parameter Corresponding States: Vapor Pressure, Enthalpies and Entropies of Vaporization, and Liquid Fugacity Coefficients," *Ind. Eng. Chem. Fundamentals*, **11**, 509 (1972).

Chang, S. D., and B. C.-Y. Lu, "A Generalized Virial Equation of State and Its Application to Vapor-Liquid Equilibria at Low Temperatures," *Adv. Cryogenic Eng.*, **17**, 255 (1972).

Chao, K. C., R. A. Greenkorn, O. Olabisi, and B. H. Hensel, "Fugacity and Vapor Pressure of Nonpolar Liquids at Low Temperatures," *AIChE J.*, **17**, 353 (1971).

Curl, Jr., R. F., and K. S. Pitzer, "Volumetric and Thermodynamic Properties of Fluids—Enthalpy, Free Energy, and Entropy," *Ind. Eng. Chem.*, **50**, 265 (1958).

Dolittle, A. K., "Some Thermodynamic Properties of n-Heptane," *Chem. Eng. Progr. Symp. Ser. No. 44*, **59**, 1 (1963).

Felsing, W. A., and G. M. Watson, "The Compressibility of Liquid *n*-Octane," *J. Am. Chem. Soc.*, **64**, 1822 (1942).

Jenkin, C. F., "Dilatation and Compressibility of Liquid Carbonic Acid," *Proc. Roy. Soc.* (London), **98**, 170 (1920).

Johnes, Jr., M. L., D. T. Mage, R. C. Faulkner, Jr., and D. L. Katz, "Measurement of the Thermodynamic Properties of Gases at Low Temperature and High Pressure-Methane," *Chem. Eng. Progr., Symp. Ser. No. 44*, **59**, 52 (1963).

Lee, B.-I., and W. C. Edmister, "Fugacity Coefficients and Isothermal Enthalpy Differences for Pure Hydrocarbon Liquids," *Ind. Eng. Chem. Fundamentals*, **10**, 229 (1971).

Lu, B. C.-Y., C. Hsi, S. D. Chang, and A. Tsang, "A Generalized Correlation of Volumetric Properties of Normal Fluids at Low Temperatures: An Extension of Pitzer's Generalized Correlation," *AIChE J.*, **19**, 748 (1973).

Olds, R. H., H. H. Reamer, B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems—Volumetric Behavior of *n*-Butane, "*Ind. Eng. Chem.*, **36**, 282 (1944).

Pitzer, K. S., D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins, and D. E. Peterson, "The Volumetric and Thermodynamic

Properties of Fluids II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization," *J. Am. Chem. Soc.*, 77, 3433 (1955).

Reamer, H. H., and B. H. Sage, "Phase Equilibria in Hydrocarbon System—Volumetric Behavior of Cyclohexane," *Chem. Eng. Data*, 1, 9 (1957).

Reid, R. C., and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd edit., pp. 272-283, McGraw-Hill, New York (1966).

Reid, R. C., and J. R. Valbert, "Derivative Compressibility Factors," *Ind. Eng. Chem. Fundamentals*, 1, 292 (1962).

Rowlinson, J. S., *Liquids and Liquid Mixtures*, 2nd edit., Ch. 2, pp. 34-51, Butterworth, London (1969).

Yen, L. C., and R. E. Alexander, "Estimation of Vapor and Liquid Enthalpies," *AIChE J.*, 11, 334 (1965).

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On Meeting the Provisions of the Clean Air Act

A general structure is proposed for determining a set of long-term (multiyear) source control measures which achieve specified levels of air quality for an airshed at least cost. Such a structure is useful in evaluating alternative air pollution abatement strategies from the standpoint of air quality and total cost. The theory is applied to the problem of evaluating sets of control actions over the period 1973-1975 in Los Angeles. Costs of achieving various levels of air quality in Los Angeles over this period are determined.

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SCOPE

The 1970 amendments to the Clean Air Act mandated clean air goals to be achieved in major urban areas. On June 15, 1973, the Administrator of the Environmental Protection Agency announced transportation control plans for 23 metropolitan areas which, if implemented, would result in substantial limitations in gasoline sales and inner city traffic in these areas by 1977. While the measures proposed would lead to reduced emissions of primary air pollutants, it is not clear that the particular elements of the control plan will lead to the desired levels of air quality and also do so at costs which are politically tolerable. A formalism which permits the systematic evaluation of the multitude of possible air pollution control strategies with respect to both air quality and total cost is highly desirable in developing implementation plans for urban regions. The presentation of such a formalism is the subject of this paper. The problem considered is to determine the set of control measures that minimizes the total cost of control while maintaining specified levels of air quality in each of a given number of years. It is assumed that an airshed model which is capable of relating atmospheric pollutant levels to source emission strengths is available. Control methods are considered for both fixed and mobile sources. The objective is to determine the least-cost allocation of existing control methods to sources in a given region such that prescribed air quality standards are not violated.

CONCLUSIONS AND SIGNIFICANCE

A general framework for the evaluation of air pollutant emission control strategies for an airshed is presented. The framework is developed so that it is applicable to an arbitrary number and type of sources, an arbitrary type of emission level/air quality model, and an arbitrary measure of air quality. Computational methods for determining the optimal set of control measures are briefly discussed. The theory is applied to the evaluation of air pollution control strategies for Los Angeles County for the period 1973 to 1975. The important primary pollutants in Los Angeles are nitric oxide and hydrocarbons, while air quality standards are based on atmospheric levels of nitrogen dioxide and ozone, both secondary pollutants. The least-cost control strategies are determined on the basis of air quality standards expressed in terms of the number of days per year that NO_2 and O_3 concentrations exceed current primary standards (0.25 and 0.10 ppm for one-hour average) in downtown Los Angeles. Use of these constraints enables use of an empirical emission level/air quality correlation developed by Trijonis (1972). It is shown that the number of days per year that the NO_2 and O_3 primary standards are violated can be reduced from the estimated 1975 level of 26 and 77 days, respectively, to 10 and 50 days at a cost of approximately 70 million dollars over the period 1973-1975.

An airshed system can be visualized to consist of a number of components: (1) Various pollutant-emitting sources, such as motor vehicles, power plants, industries, aircraft, etc. (2) Various chemical species, that is, pollutants. The primary pollutants, which are emitted directly from sources, consist predominantly of carbon monoxide (CO), hydrocarbons, nitrogen oxides (NO_x), SO_2, and particulate matter. The secondary pollutants, formed by atmospheric chemical reactions, consist of O_3, NO_2, sulfates, nitrates, and organic compounds. (3) A multitude of control methods for abating the emissions of the various sources. (For example, motor vehicle emissions can be abated through the use of evaporative control systems, catalytic mufflers, etc. Emissions from power plants can be controlled by burner modifications, substitution of natural gas for fuel oil, etc.) (4) Meteorological param-